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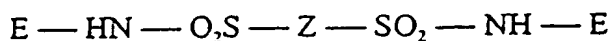
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The present invention concerns polyethylene containing bridge-type bonds and polyethylene elastomer mixtures containing bridge-type bonds with improved properties. In particular, this invention concerns polyethylene and polyethylene elastomer mixtures that contain bridges formed by sulfonamide groups.

New developments in the field of polymerization have made possible the production of ethylene polymerizates, including mixtures with other polymerizates that are valuable for a variety of applications. These ethylene polymerizates are not satisfactory in the crude state with respect to various properties, like hardness, rigidity, ambient stress rupture, gas permeability, solvent permeability, melt strength at low shear load, etc. It is known to one skilled in the art that these polymerizates can be crosslinked, for example with peroxides, in order to alter their properties. Such crosslinked polymerizates are deformable by pressure and extraordinarily useful in the applications in which resistance to solvents and elevated temperatures is important. After crosslinking they are insoluble and can no longer be considered thermoplastics, which are capable of being extruded, injection molded or processed by other methods in which melt flow is essential.

It has now been found that ethylene polymerizates can be produced with sulfonamide group bridges in which these polymerizates are fully soluble in ordinary polyethylene solvents, but exhibit greater resistance to ambient stress rupture or cracks, greater hardness, rigidity, higher melt resistance at low shear load and lower permeability of gases and liquids. These polymerizates containing bridges can be smoothly extruded with improved dimensional stability, owing to their higher melt strength and can be heat-deformed into a number of useful articles.

Accordingly, the present invention concerns a solid thermoplastic polyethylene containing sulfonamide bridges with the structure



in which E is polyethylene and Z an organic group that is free of hindering groups in which said sulfonamide bridges make up about 0.001 wt% to about 0.075 wt%, referred to the total weight of the polymerizate containing bridges. The expression "free of hindering groups" means that Z contains no group that could adversely affect the reaction forming the bridges. For example, Z can contain one or more free sulfonazide groups, which are not hindering groups, however. The ethylene polymerizate containing bridge type bonds of this invention is fully soluble in

perchloroethylene at a temperature of 110°C and can be smoothly extruded and heat-deformed at temperatures that are slightly higher than those of a polymerizate not containing bridges. The peculiar ethylene polymerizates containing bridge-type bonds of this invention begin to crystallize at a higher temperature and crystallization occurs more quickly than with polyethylene not containing bridge-type bonds. The resulting crystallized polymerizate containing bridge bonds has higher density and a clearly recognizable improvement with respect to ambient stress rupture.

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Any linear polyethylene, including mixtures of linear polyethylene with about 1% to about 25% of an elastomeric hydrocarbon polymerizate having no more than about 5 wt% unsaturation and in the most preferable case fully unsaturated, can be used to produce the polyethylene containing bridge bonds according to this invention. Examples of elastomeric hydrocarbon polymerizates that can be mixed with polyethylene are polyisobutylene, butyl rubber, ethylene-propylene copolymerizate, ethylene-propylene-dicyclopentadiene terpolymerizate, etc.

Any polysulfonazide, i.e., any compound of the general formula $R(SO_2N_3)_x$, in which R is an organic group inert relative to the bridge formation reaction, and x is about 2 to 8, can be used. Preferably x has an average value of about 2 and R can be chosen from the group of organic groups consisting of alkylene, halogenated alkylene, arylene, aralkylene and alkarylene residues. Examples of polysulfonazides are alkylsulfonazides, like 1,5-pentane-bis(sulfonazide), 1,8-octane-bis(sulfonazide), 1,10-decane-bis(sulfonazide), 1,10-octadecane-bis(sulfonazide), etc., aryl-bis(sulfonazides), like 1,3-benzene-bis(sulfonazide), 4,4'-diphenylmethane-bis(sulfonazide), 4,4'-diphenyl-bis(sulfonazide), 1-octyl-2,4,6-benzene-tris(sulfonazide), 4,4'-diphenyl ether-bis(sulfonazide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene-bis(sulfonazide), etc. and mixed sulfonazides of chlorinated aliphatic hydrocarbons with an average content of about 1 to 8 chlorine atoms and 2 to 5 sulfonazide groups per molecule.

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The bridge-forming reaction is run by heating the ethylene polymerizate in the presence of polysulfonazide to a temperature at which the sulfonazide decomposes, i.e., generally in the range of about 100 to 250°C. The amount of employed polysulfonazide will be sufficient to produce the polymerizate containing bridges with about 0.001 wt% to about 0.075 wt% sulfonazide bridges.

The polysulfonazide bridge-forming agent can be incorporated in the ethylene polymerizate by numerous procedures. For example, it can be uniformly mixed by simple grinding on an ordinary rubber mill, by extrusion or dissolved in a solution or dispersion containing a polymerizate. In any of these methods the bridge-forming agent is distributed in the entire polymerizate and uniform bridge formation is achieved when the mixture is heated.

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The ethylene polymerizates containing bridge bonds of the present invention can contain additives, like extenders, fillers, pigments, stabilizers, plasticizers, fire retardants, etc. However, there are many cases in which an ethylene polymerizates containing bridge bonds with an additive is not required or desired and excellent products are obtained to which nothing other is added than a bridge-forming agent.

The following examples are provided to explain the peculiar ethylene polymerizates containing bridge bonds according to this invention. All parts and percentages are understood to mean by weight unless otherwise mentioned. |

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Examples 1-3

In each example 100 parts of a finely distributed linear polyethylene with a density of 0.945 and a melt flow index of 0.3 was wetted with acetone, which contained the desired amount of polysulfonazide bridge-forming agent and 0.1 part 4'-thiobis(3-methyl-6-tert-butylphenol) stabilizer. A mixture of sulfonazide of a chlorinated aliphatic hydrocarbon with an average content of 11 carbon atoms, two chlorine atoms and two sulfonazide groups per molecule was used as bridge-forming agent. The acetone was evaporated during agitation and the resulting powder dried under vacuum at a temperature of 60° C. Each powdered mixture was introduced to a 1 1/4" extruder with a 20:1 length:diameter ratio, a screw speed of 35 rpm and a temperature gradient over the length of the cylinder of 360° to 430° F. The extrudate was immersed in the form of strands from a 0.125" spray nozzle into a water bath. The resulting extrudates were investigated with respect to surface smoothness, weighed to determine extrusion speed and cut into pellets. The pellets of each preparation were compression molded at a temperature of 347° F for 8 minutes under a pressure of 500 psi into 4" x 4" x 0.075" sheets and investigated for resistance to the occurrence of ambient stress ruptures or cracks during bending by 180° during immersion in an aqueous solution of nonylphenol-ethylene oxide adduct (nonionic detergent).

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The results of the investigations during extrusion and resistance to ambient stress ruptures are listed in Table 1.

Table 1.

Example No.	Sulfonazide, parts/100	Extrusion speed, g/min	Extrudate surface	Extrudate density	Resistance to ambient stress ruptures in hours		
					20% rupture	50% rupture	90% rupture
1	0	97	smooth	0.9390	80	112	142
2	0.03	98	smooth	0.9395	116	152	207
3	0.05	101	smooth	0.9404	164	208	268

It is apparent from the aforesaid that bridge formation of polyethylene with polysulfonazides causes a significant improvement in terms of ambient stress ruptures without affecting the extrudate surface quality or extrusion speed.

Example 4

The polyethylene described in examples 1-3 was mixed with 1,3-benzene-bis(sulfonazide) and 4,4'-thiobis-(3-methyl-6-tert-butylphenol) stabilizer, precisely as described in examples 1-3. Part of the pulverized mixture was extruded into strands as described in examples 1-3. The resulting strands were evaluated with respect to surface roughness and extrusion speed and then cut into pellets to determine the melt flow index. Another part of the mixture was extruded downward through a crosshead drawing die and investigated with respect to dimensional stability by the following method. After 12" of the polymerizate strand had been extruded, this was taken off at the spray nozzle with forceps and then allowed to cool, suspending it vertically. The length increase of the cooled strand in comparison with the original 12" length was the gauge of dimensional stability. This gauge is a feature pertaining to melt (softening) strength under limited shear load. A control sample of the polyethylene was mixed in the same manner and investigated, except that the disulfonazide was left out. The results of the investigations are shown in the following table.

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	Example 4	Control sample
1,3-Benzene-bis(sulfonazide)	0.03	0
Melt flow index (I_2 at 190°C)	0.23	0.31
Extrudate surface	smooth	smooth
Extrusion rate, g/min	99	98
Percent dimensional stability	1.5	14.7

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Examples 5-7

Samples of the pellets described in examples 1-3 were extruded as parison using a 1½" extruder at a temperature of 410°F and a screw speed of 45 rpm and the resulting parison was blown in the form of 4 oz. standard Boston round bottles. Better shape retention of the parison was observed in the preparations containing polysulfonazide, which resulted in more uniform wall thickness from the top to bottom of the bottles. Parts of the side walls of the bottles were investigated with respect to density and bending rigidity. Results are shown in Table 2.

Table 2.

Example No.	Sulfonazide, parts/100	Density of bottle wall	Bending rigidity, psi
5	0	0.9459	70,000
6	0.03	0.9475	77,000
7	0.05	0.9478	77,500

Examples 8-10

The compression molded pellets containing different amounts of polysulfonazide were produced as described in examples 1-3. The mixed sulfonazide described in example 1-3 was used as bridge-forming agent. Pellets of each compression molding preparation were investigated with respect to melt flow index and then molded by injection molding in a helical compression mold at a temperature of 390°F using a pressure of 800 psi. The concentration of polysulfonazide, the melt flow index and the length of the spiral produced by injection molding for each preparation are shown in Table 3.

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Table 3.

Example No.	Sulfonazide, part/100	Melt flow index (I ₂ at 190°C)	Spiral length (mm)
8	0	0.27	108
9	0.025	0.21	112
10	0.050	0.12	108

It is apparent from the aforesaid that, despite the significant reduction in melt flow index, which was caused by the bridge-forming reaction, no significant difference was found with respect to melt flow within the helical casting mold under equally high shear load conditions. |

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Examples 11 and 12

In each example 100 parts of a finely divided linear polyethylene with a density of 0.945 and a molecular weight of about 150,000 was wetted with acetone, which contained the desired amount of polysulfonazide and 0.1 part 4,4'-thiobis(3-methyl-6-tert-butylphenol) stabilizer. The mixed sulfonazide described in examples 1-3 was used as a bridge forming agent. The acetone was evaporated during agitation and the resulting powder dried under vacuum at a temperature of 60°C. Each pulverized mixture was ground on a two-roll rolling table for 12 minutes at a temperature of 340°F and then cut into pellets. Each set of pellets was injection molded into tensile elements at a cylinder temperature of 450°F and 800 psi pressure. The melt flow indices of the pellets and the properties of the elements produced by injection molding are shown in the following table.

	Example number	
	11	12
Sulfonazide, parts/100	0	0.05
Melt flow index (I_2 at 190°C)	0.15	0.08
Density of molded articles	0.9455	0.9461
Tensile strength (psi)	6060	6800
Tensile modulus	134,000	154,000

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It is apparent from the aforesaid that the polymerizate having polysulfonazide bridges can be processed just as readily as the polymerizate having no bridges and exhibits higher density, strength and rigidity.

Examples 13 and 14

In each example a linear polyethylene with a temper density of 0.957, a molecular weight of 147,000 and no detectable unsaturation was mixed with a polysulfonazide, extruded and cut into pellets, as described in examples 1-3. The mixed sulfonazide described in examples 1-3 was used as bridge forming agent. A percentage of the pellets was compression molded into 0.075" sheets at 350°F for 10 minutes under 800 psi pressure and tested with respect to bending agility. Another portion of the pellets was injection molded in a helical mold as described in examples 8 to 10. The results of these investigations are shown below.

	Example number	
	13	14
Sulfonazide, parts/100	0	0.075
Extrudate surface	smooth	smooth
Extrusion speed (g/min)	105	104
Melt flow index (I_2 at 190°C)	0.75	0.22
Density of molded product	0.9470	0.9510
Bending rigidity of molded product	73.500	86.500
Spiral length (mm)	90	88

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It is apparent from the aforesaid that bridge formation in unsaturated linear polyethylene resulted in improved density and rigidity without adversely affecting the flow properties during extrusion.

Examples 15-24

To record the critical structure of polysulfonazide bridge-forming agents, samples of linear polyethylene with a density of 0.945 and a melt flow index of 0.30 were mixed with different amounts, either with 1,10-decanedisulfonazide or a commercial peroxide crosslinking agent. Each sample was mixed, extruded and cut into pellets as described in examples 1-3. Part of each extrudate was introduced to a water cooling bath, evaluated with respect to surface conditions, cut into pellets and then evaluated with respect to melt flow index. Another part was extruded without cooling and investigated with respect to dimensional stability as described in example 4. The results of these investigations are shown in Table 4. p. 15

Table 4.

Examp le No.	Additive	Additive, part/100	Extrudate appearance	Melt flow index	% dimensional stability
15	-	0	smooth	0.33	14.6
16	1,10-decanedisulfonazide	0.010	smooth	0.30	6.1
17	1,10-decanedisulfonazide	0.020	smooth	0.27	2.0
18	1,10-decanedisulfonazide	0.030	smooth	0.25	0
19	1,10-decanedisulfonazide	0.050	smooth	0.21	-2.0
20	2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne	0.001	somewhat rough	0.24	5.0
21	2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne	0.005	somewhat rough	0.20	2.0
22	2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne	0.010	rough	0.17	0
23	2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne	0.020	rough	0.12	-1.4
24	2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne	0.030	very rough	0.10	-3.0

Surprising differences between the effects of the two additives on the rheological properties of polyethylene are apparent from the above. At equal concentrations the peroxide causes a greater reduction in melt flow index and an improvement in dimensional stability, but causes roughness of the extrudate, even in amounts as little as 0.01 part/100.

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Examples 25 and 26

Examples 11 and 12 are repeated, except that in each case 10 parts polyisobutylene (with a molecular weight of 90,000) per 100 parts polyethylene was added during production of the compound on a two-roll rolling table. The results of the investigations on these mixtures containing bridges are listed below.

	Example number	
	25	26
Sulfonazide, parts/100	0	0.05
Density of molded article	0.9475	0.9498
Tensile strength (psi)	5450	5900
Tensile modulus (psi)	115,000	133,000

The polyethylene polymerizates containing bridges of this invention are useable in a number of applications, as in blow molding, paper coating methods, vacuum molding and other applications where more limited heat effects or shape changes are required. Their higher density and rigidity permits their use in bottles, films and packaging materials. The improved resistance to stress rupture or cracking is of particular importance in bottles for detergents, wire and cable insulation and in pipelines.

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Claims

1. Method for production of solid plastic polyethylenes containing bridge bonds, characterized by heating of the mixture of ethylene polymer and about 0.01 to 0.075 wt% (referred to polyethylene) of a sulfonazide, which has the general formula $R(SO_2N_x)_x$, in which R is an organic radical, which is inert relative to the bridge formation reactions and x is a whole number from 2 to 8.
2. Method according to Claim 1, characterized by the fact that the mixture is heated to a temperature at which the sulfonazide decomposes.
3. Method according to Claim 1 or 2, characterized by the fact that the mixture is heated to a temperature of 100 to 250° C.
4. Method according to any of the Claims 1-3, characterized by the fact that the polyethylene is linear polyethylene or a mixture of polyethylene with polyisobutylene.